

# Supplementary Materials: An Unusual Stress Metabolite Induced by Cobalt from a Hydrothermal Vent Fungus *Aspergillus* sp. WU 243

Chihong Ding, Xiaodan Wu, Bibi Nazia Auckloo, Chen-Tung Arthur Chen, Ying Ye, Kuiwu Wang and Bin Wu

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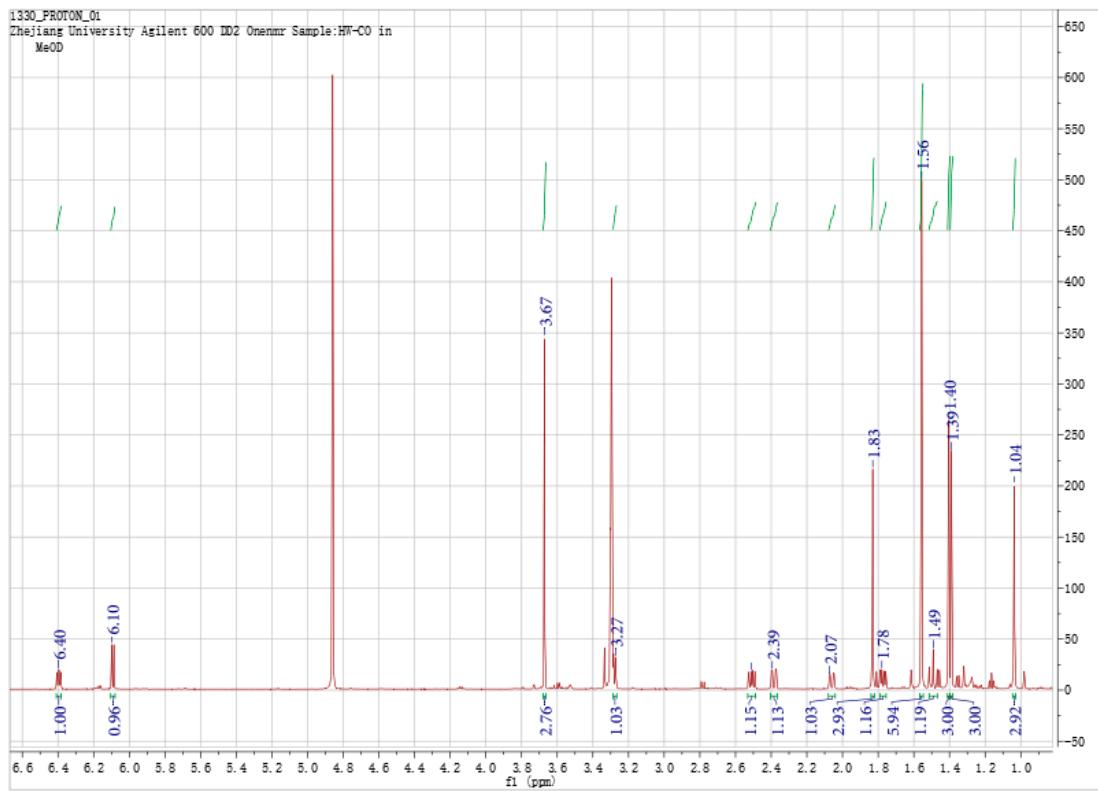
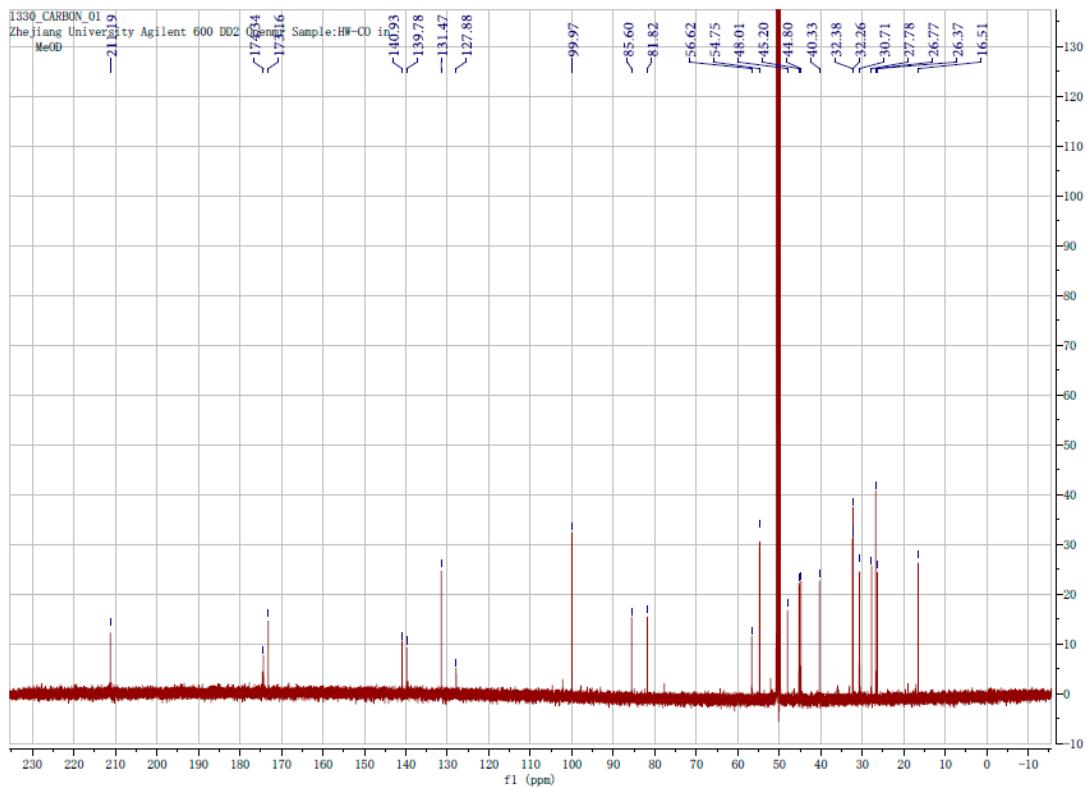
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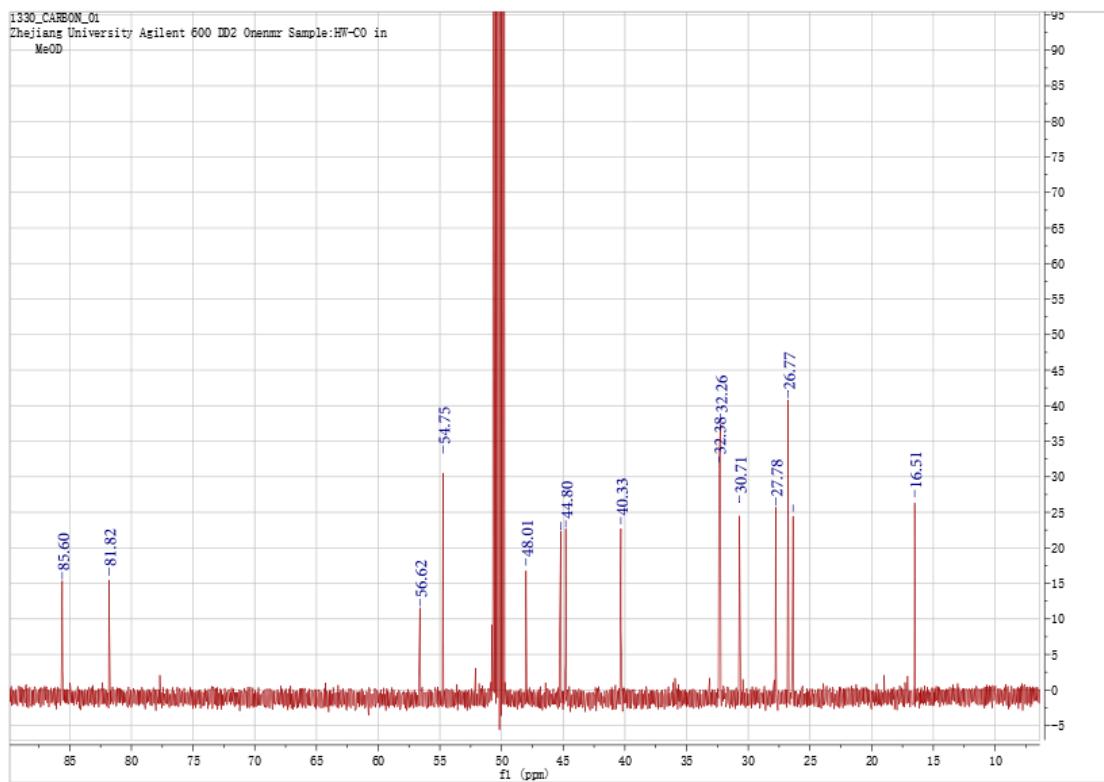
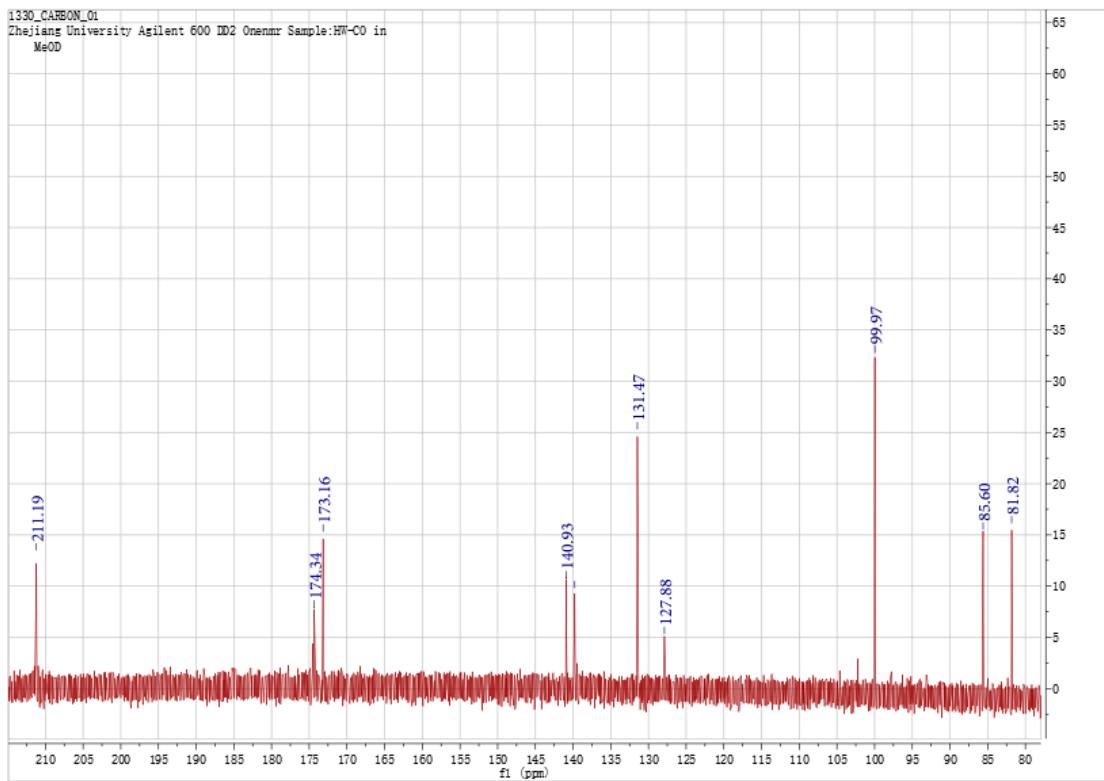
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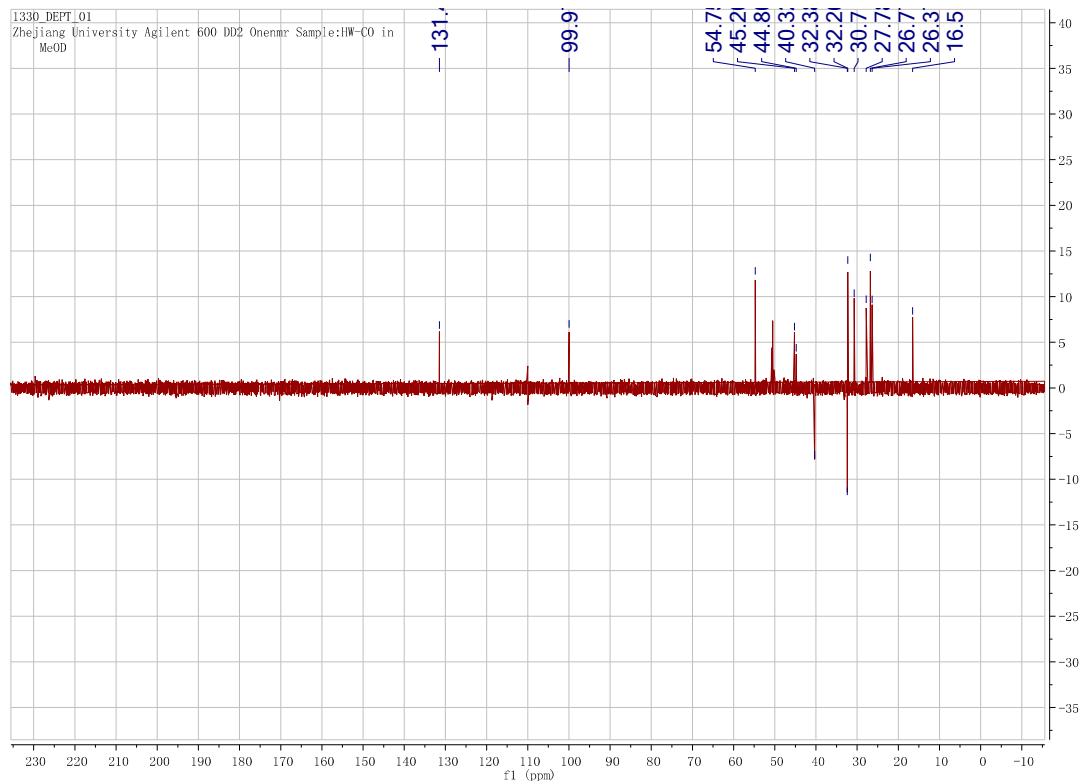
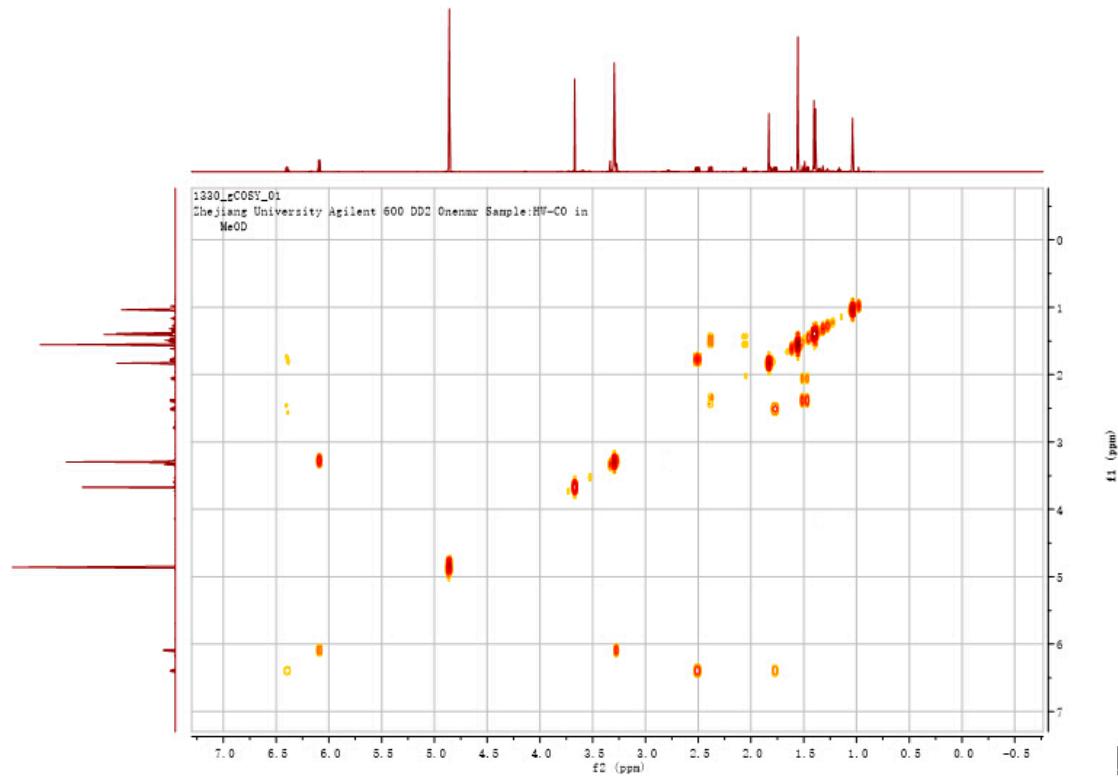
**Table S2.**  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR ( $\text{CD}_3\text{OD}-d_4$ , 500 MHz) data for known compound cyclo-(L-tryptophyl-L-phenylalanyl).

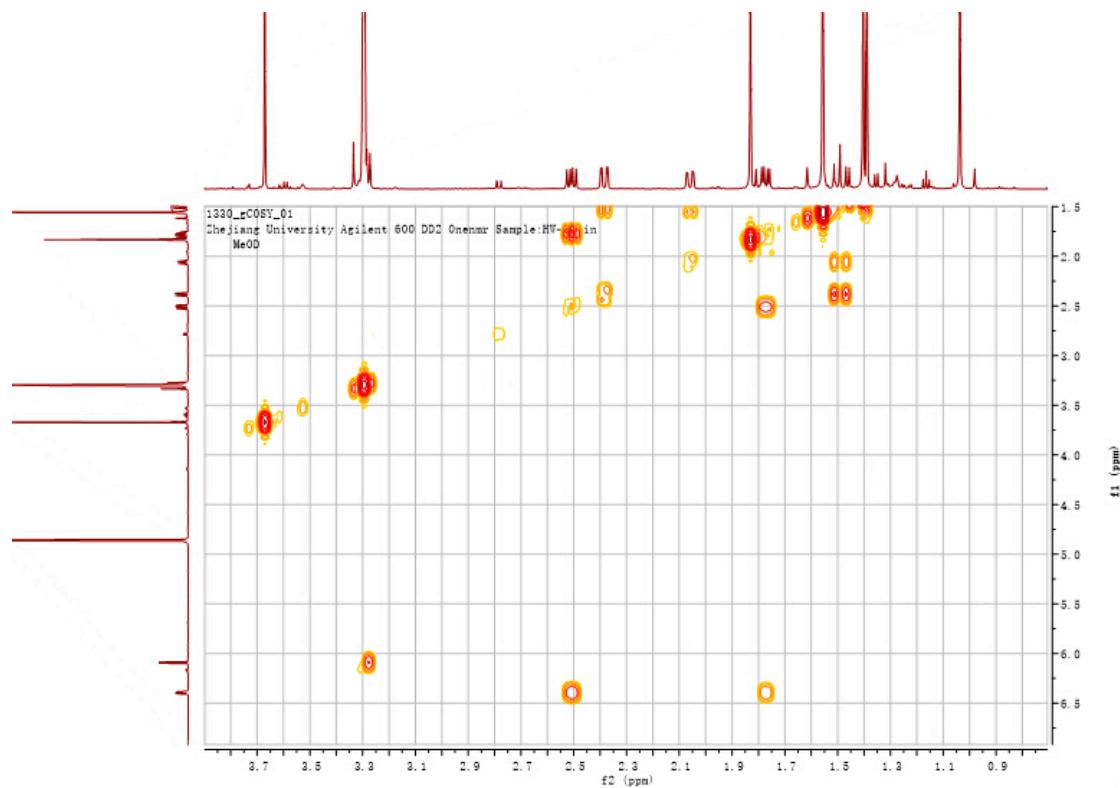
**Table S3.**  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR ( $\text{CD}_3\text{OD}-d_4$ , 500 MHz) data for known compound cordyol C.

**Table S4.**  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR ( $\text{CD}_3\text{OD}-d_4$ , 500 MHz) data for known compound sydonic acid.

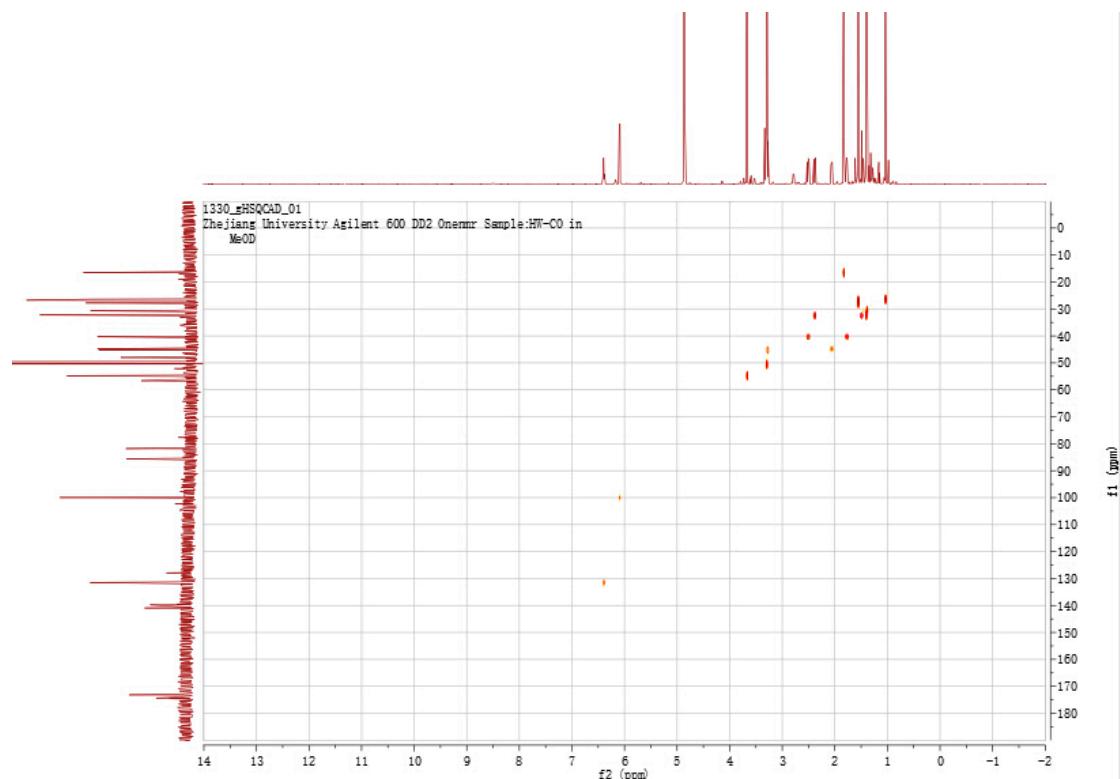
**Figure S1.**  $^1\text{H}$ -NMR spectrum for compound 1.**Figure S2.**  $^{13}\text{C}$ -NMR spectrum for compound 1.

**Figure S3.** Partially enlarged detail of  $^{13}\text{C}$ -NMR spectrum for compound **1**.**Figure S4.** Partially enlarged detail of  $^{13}\text{C}$ -NMR spectrum for compound **1**.

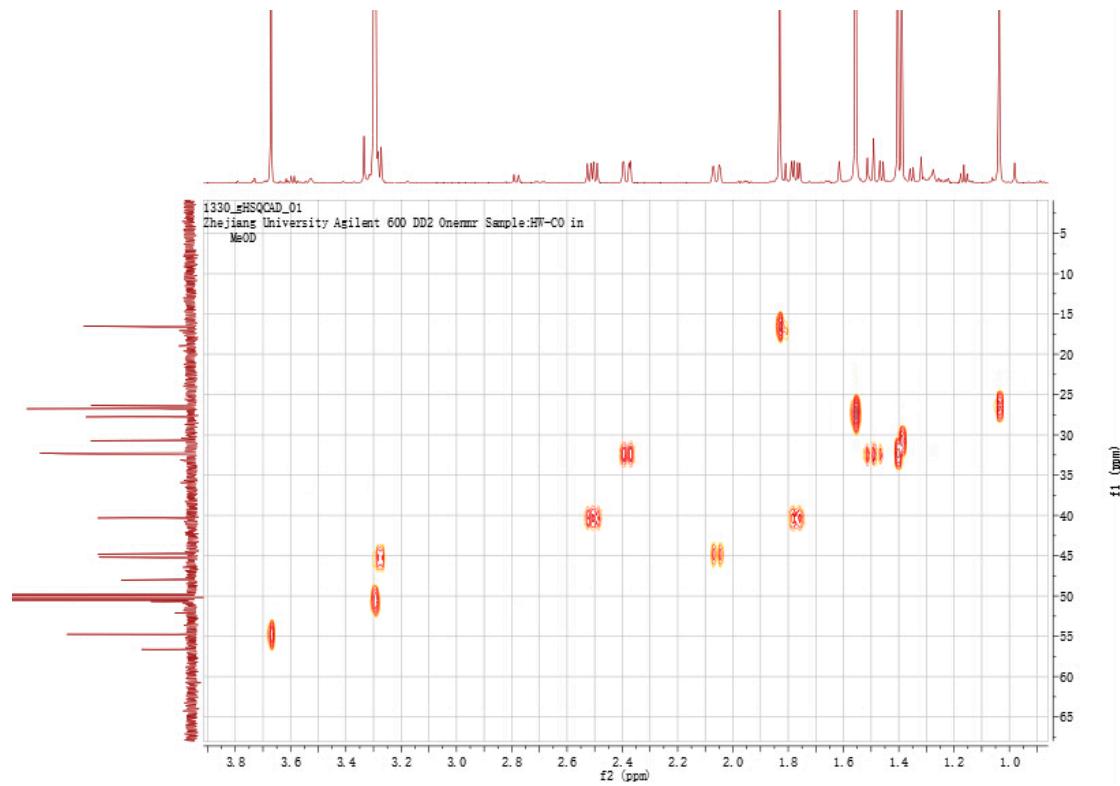
**Figure S5.** DEPT spectrum for compound 1.**Figure S6.** COSY spectrum for compound 1.



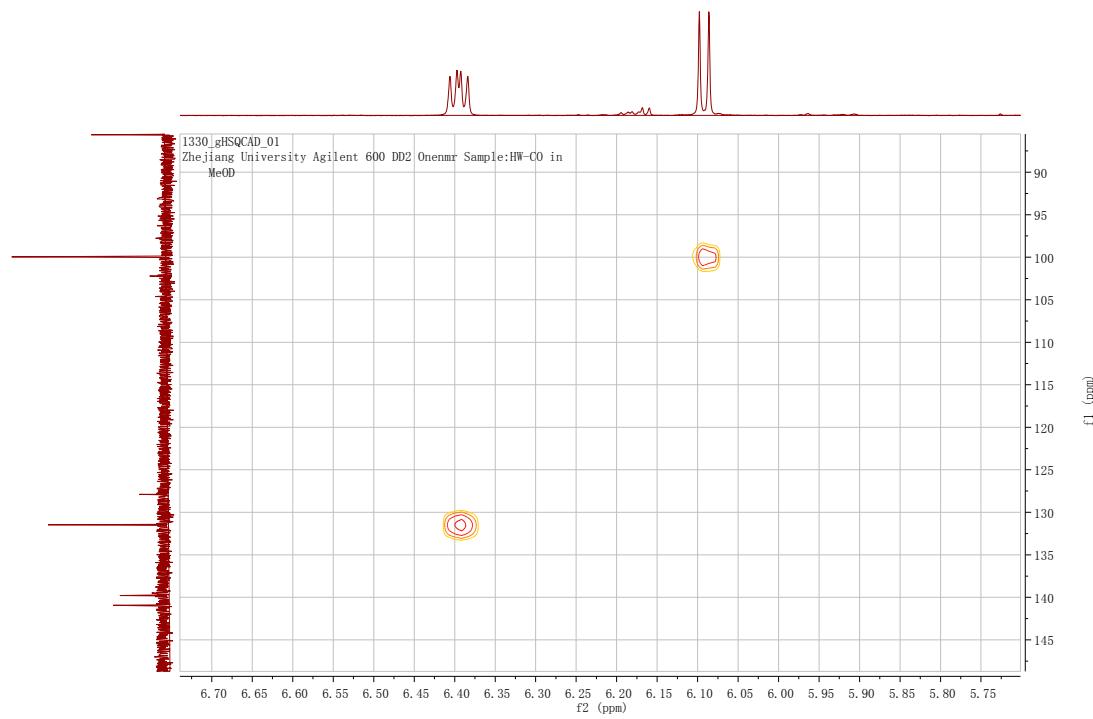
**Figure S7.** Partially enlarged detail of COSY spectrum for compound 1.



**Figure S8.** HSQC spectrum for compound 1.



**Figure S9.** Partially enlarged detail of HSQC spectrum for compound **1**.



**Figure S10.** Partially enlarged detail of HSQC spectrum for compound **1**.

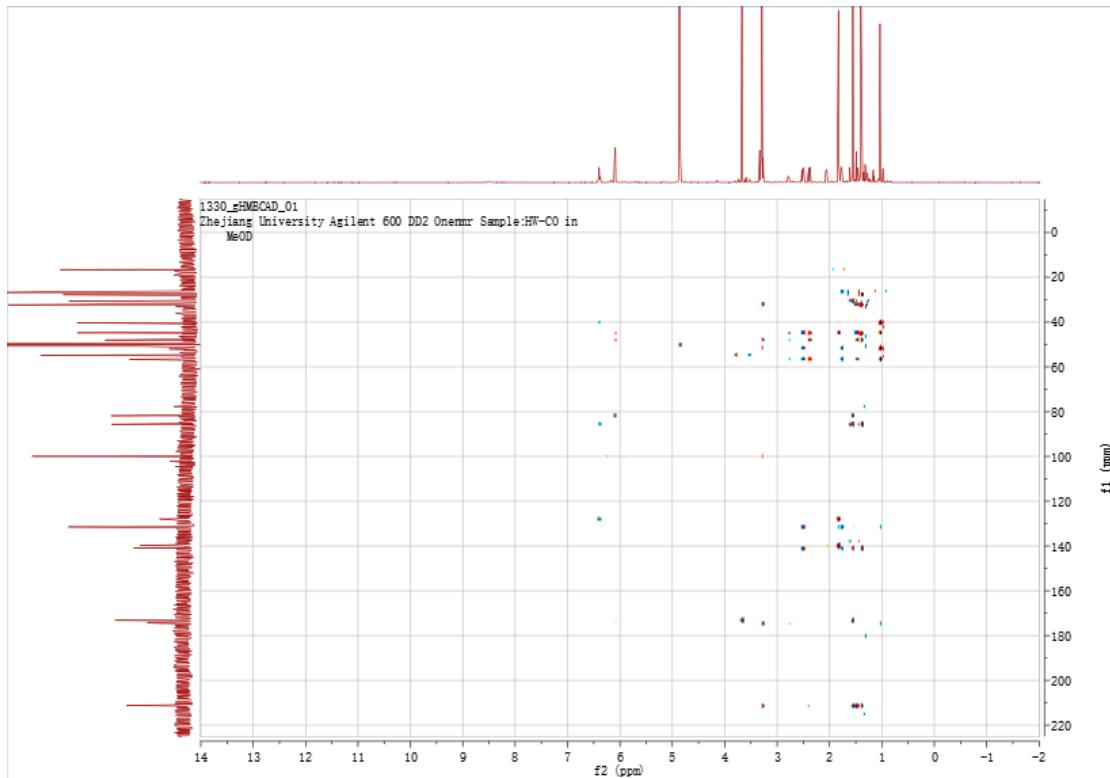


Figure S11. HMBC spectrum for compound 1.

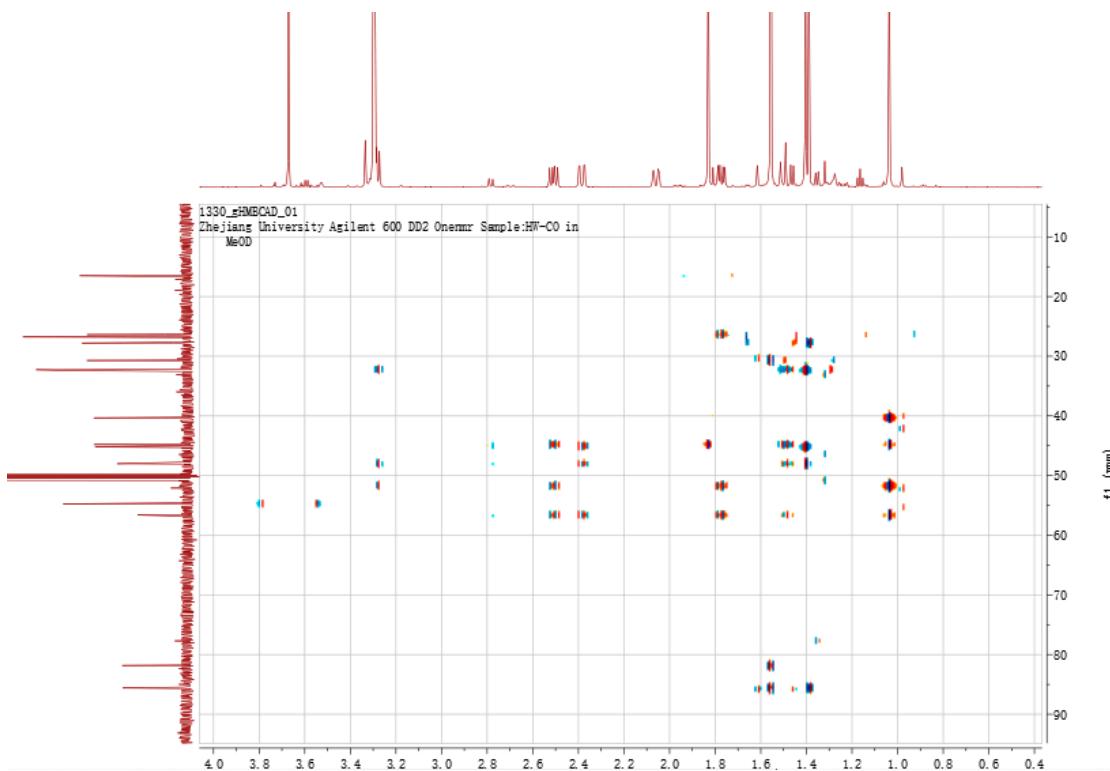
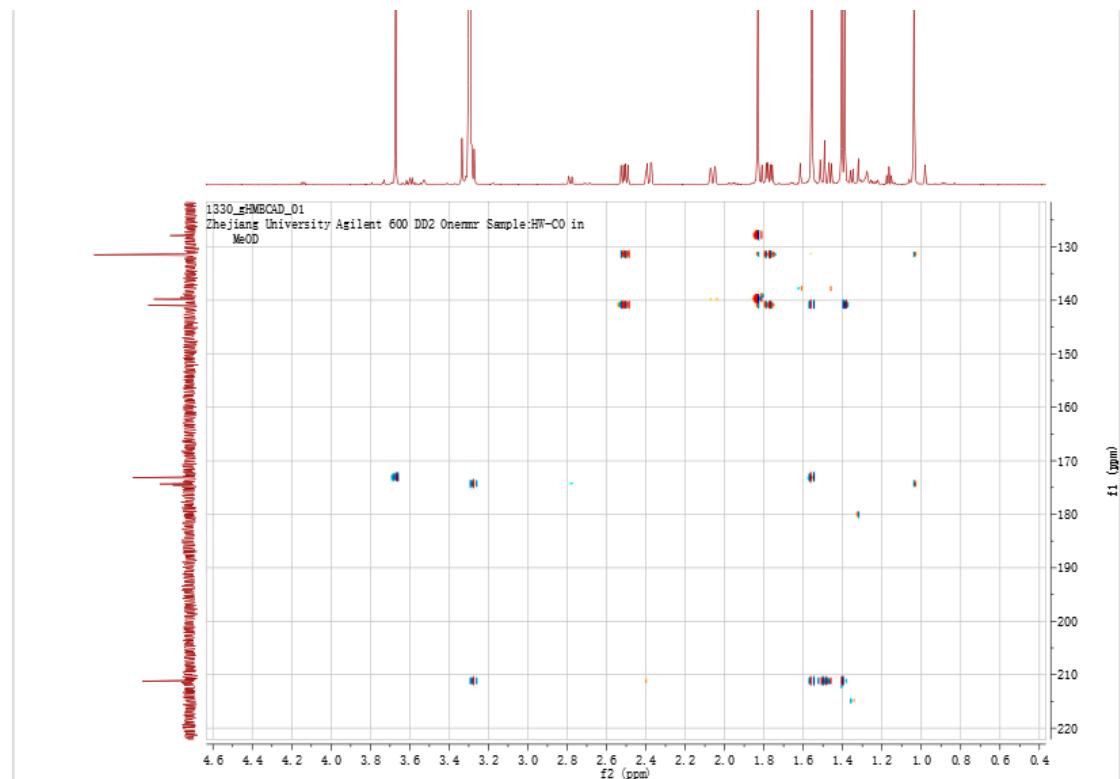
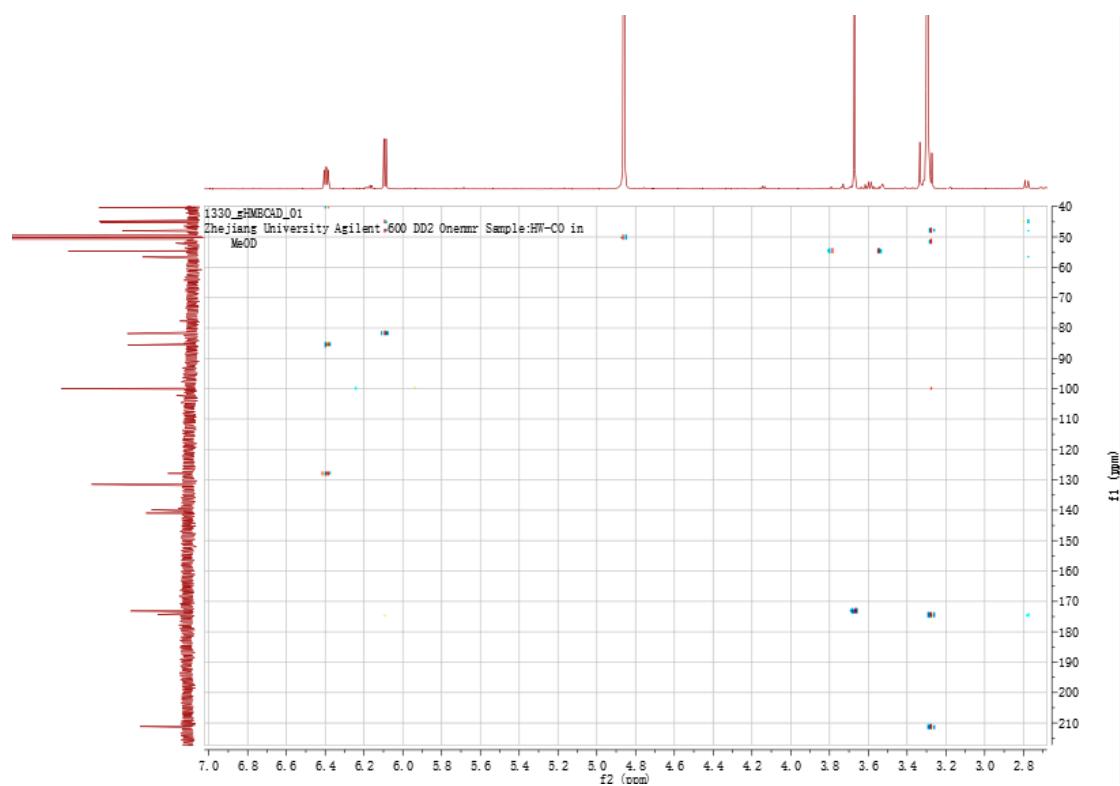


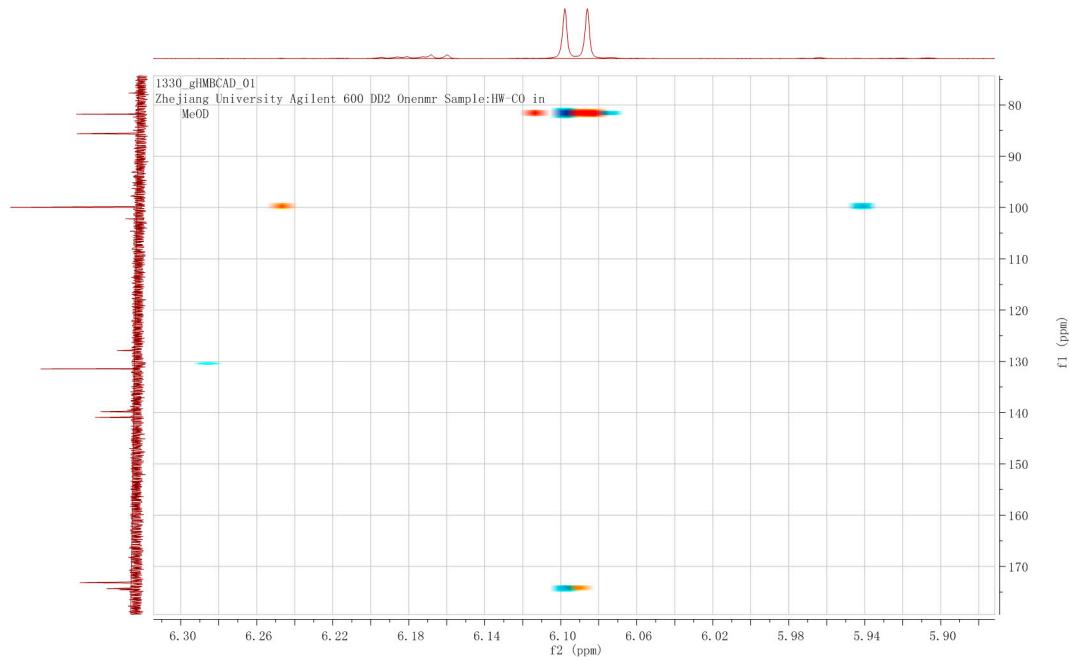
Figure S12. Partially enlarged detail of HMBC spectrum for compound 1.



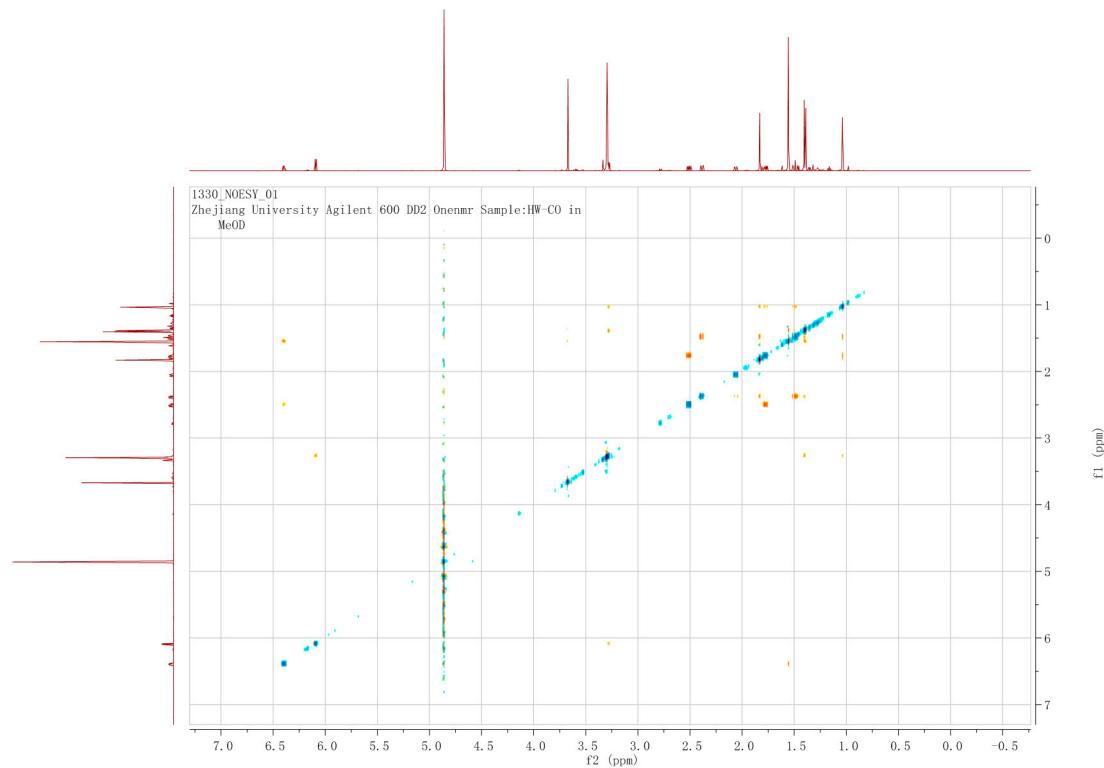
**Figure S13.** Partially enlarged detail of HMBC spectrum for compound 1.



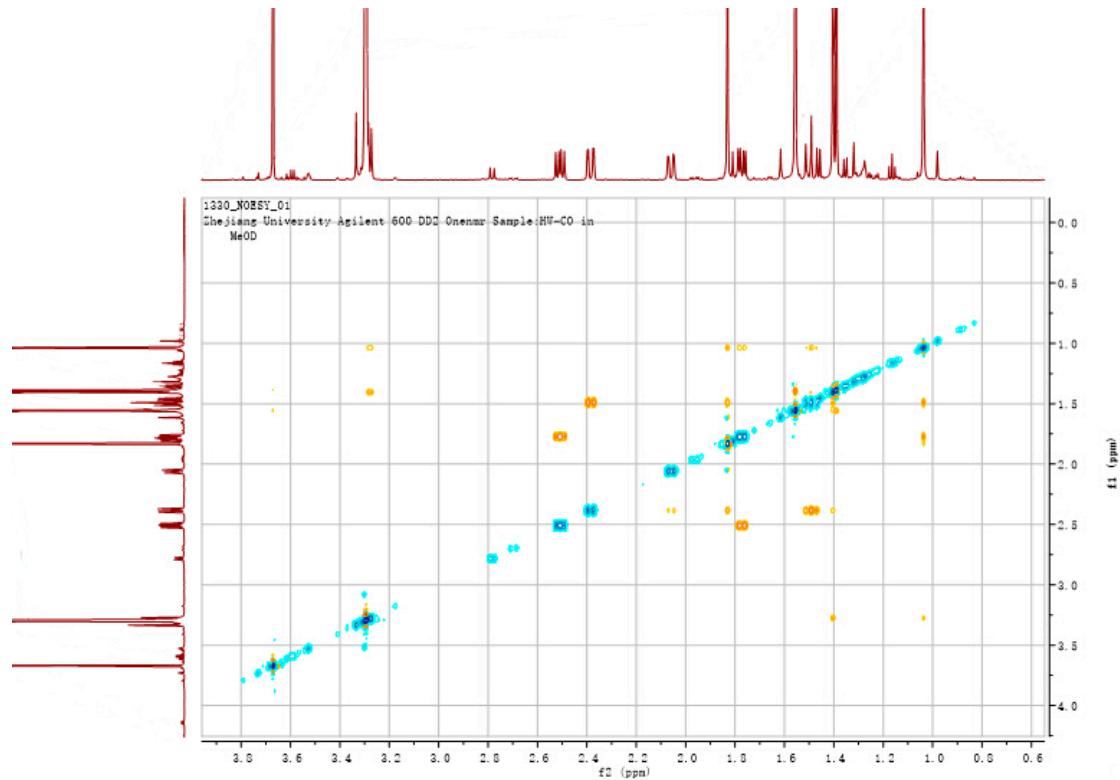
**Figure S14.** Partially enlarged detail of HMBC spectrum for compound 1.



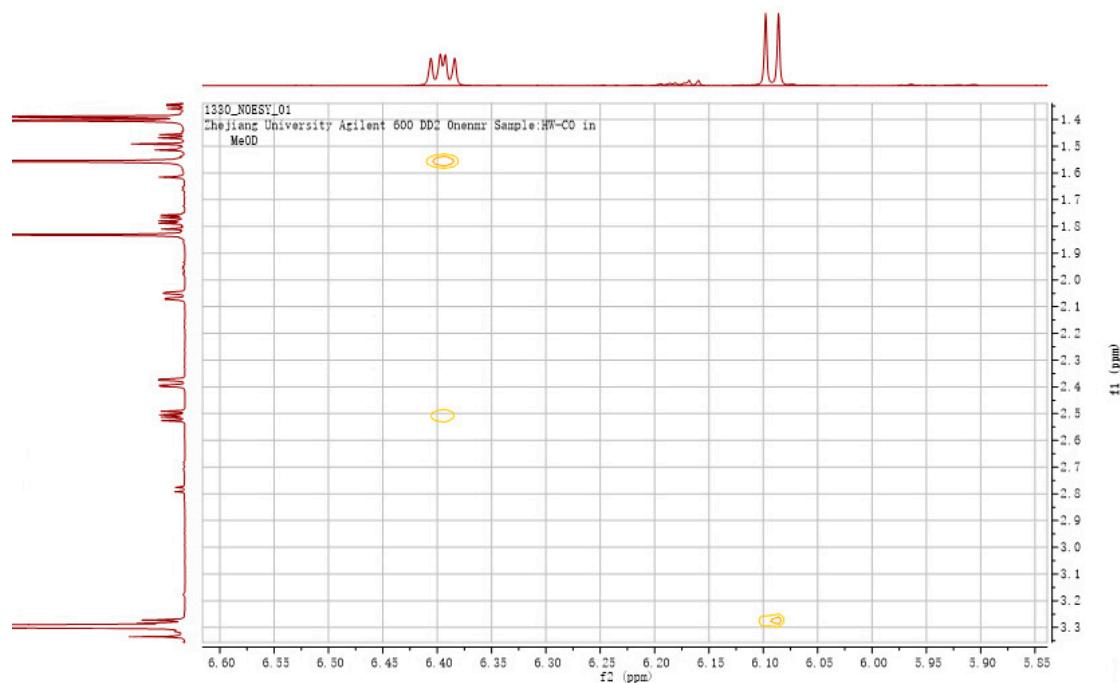
**Figure S15.** Partially enlarged detail of HMBC spectrum for compound 1.



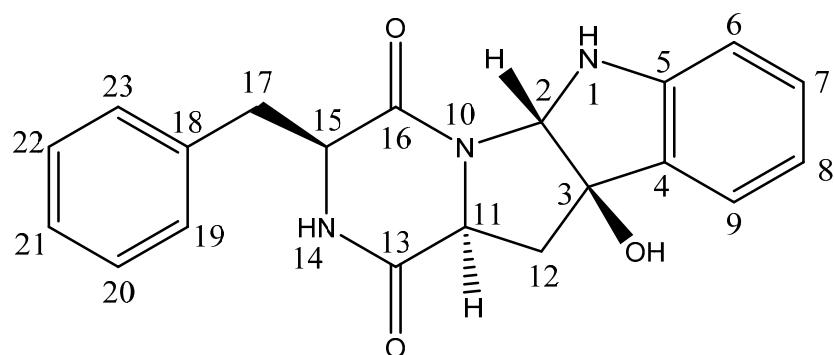
**Figure S16.** NOESY spectrum for compound 1.



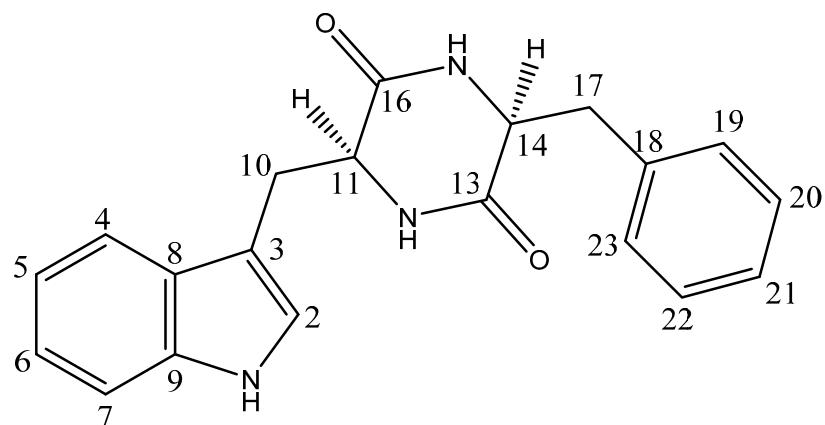
**Figure S17.** Partially enlarged detail of NOESY spectrum for compound 1.



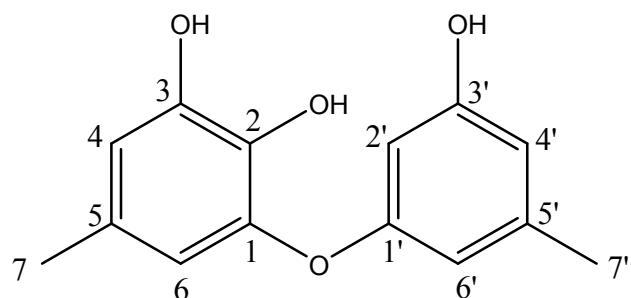
**Figure S18.** Partially enlarged detail of NOESY spectrum for compound 1.



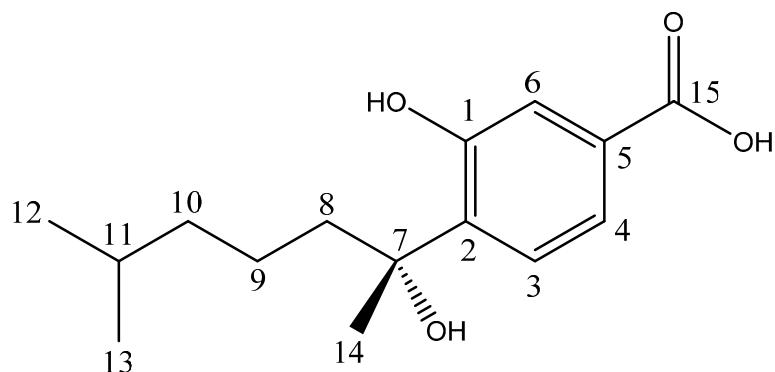
**Figure S19.** Structure of normal main product ditryptophenaline.



**Figure S20.** Structure of known compound Cyclo-(L-tryptophyl-L-phenylalanyl).



**Figure S21.** Structure of known compound Cordyol C.



**Figure S22.** Structure of known compound sydonic acid.

**Table S1.**  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR ( $\text{CD}_3\text{OD}-d_4$ , 500 MHz) data for known compound ditryptophenaline.

Position	$\delta_{\text{H}}$ ( $J$ in Hz)	$\delta_{\text{C}}$ (mult.)
1	N	--
2	4.90(s)	79.45 (CH)
3	--	56.64 (C)
4	--	130.12 (C)
5	--	149.12 (C)
6	6.69 (d,7.8)	109.25 (CH)
7	6.96 (m)	126.23 (CH)
8	6.77 (ddd,0.8,7.4,7.4)	119.02 (CH)
9	7.32 (d,7.4)	124.74 (CH)
10	N	--
11	3.99 (ddd,1.5,8.7,8.7) 3.06 (m)	56.24 (CH)
12	2.66 (dd, 1.5,8.7)	36.45 ( $\text{CH}_2$ )
13	--	169.14 (C)
14	N	--
15	4.19 (ddd,1.6,5,5)	59.70 (CH)
16	--	167.57 (C)
17	3.06 (m)	36.01 ( $\text{CH}_2$ )
18	--	135.45 (C)
19,23	7.03 (m)	127.86 (CH)
20,22	6.96 (m)	129.06 (CH)
21	7.14 (ddd,0.9,7.8,7.8)	125.15 (CH)

**Table S2.**  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR ( $\text{CD}_3\text{OD}-d_4$ , 500 MHz) data for known compound Cyclo-(L-tryptophyl-L-phenylalanyl).

Position	$\delta_{\text{H}}$ ( $J$ in Hz)	$\delta_{\text{C}}$ (mult.)
1	10.89 (s)	--
2	6.96 (d, 2)	120.83 (CH)
3	--	108.76 (C)
4	7.48 (dd, 8, 8)	118.37 (CH)
5	6.98 (ddd, 8, 8, 1.5)	118.71 (CH)
6	7.07 (ddd, 8, 8, 1)	124.37 (CH)
7	7.32 (dd, 8, 8)	111.29 (CH)
8	1.80 (m)	127.49 (C)
9	1.14 (m)	136.01 (C)
10	2.80 (dd, 14.5, 4.5)	29.66 ( $\text{CH}_2$ )
11	3.97 (m)	55.23 (CH)
12	7.91 (d, 1.5)	--
13	--	166.13 (C)
14	3.86 (m)	55.58 (CH)
15	7.72 (d, 2)	--
16	--	166.77 (C)
17	1.86 (m)	39.70 ( $\text{CH}_2$ )
18	--	136.51 (C)
19,23	7.16 (m)	127.99 (CH)
20,22	6.71 (m)	129.66 (CH)
21	7.17 (m)	126.32 (CH)

**Table S3.**  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR ( $\text{CD}_3\text{OD}-d_4$ , 500 MHz) data for known compound Cordyol C.

Position	$\delta_{\text{H}}$ ( $J$ in Hz)	$\delta_{\text{C}}$ (mult)
1	--	145.15 (C)
2	--	135.76 (C)
3	--	147.49 (C)
4	6.45 (d, 1.5)	112.84 (CH)
5		129.87 (C)
6	6.24 (d, 1.5)	113.24 (CH)
7	2.14 (s)	20.70 ( $\text{CH}_3$ )
1'	--	160.35 (C)
2'	6.16 (dd, 2, 2)	102.56 (CH)
3'	--	159.18 (C)
4'	6.29 (br s)	111.02 (CH)
5'	--	141.14 (C)
6'	6.21 (br s)	110.02 (CH)
7'	2.20 (s)	21.37 ( $\text{CH}_3$ )

**Table S4.**  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR ( $\text{CD}_3\text{OD}-d_4$ , 500 MHz) data for known compound Sydonic acid.

Position	$\delta_{\text{H}}$ ( $J$ in Hz)	$\delta_{\text{C}}$ (mult.)
1	--	155.94 (C)
2	--	135.36 (C)
3	7.06 (d, 8.0)	126.33 (CH)
4	7.52 (d, 8.0)	121.14 (CH)
5		129.94 (C)
6	7.53 (s)	119.18 (CH)
7	--	78.85 (C)
8	1.80 (m)	42.81 (CH)
9	1.14 (m)	21.62 ( $\text{CH}_2$ )
10	1.28 (m)	38.99 ( $\text{CH}_2$ )
11	1.49 (m)	27.75 (CH)
12	0.82 (d, 6.5)	22.52 ( $\text{CH}_3$ )
13		22.50 ( $\text{CH}_3$ )
14	1.66 (s)	28.76 ( $\text{CH}_3$ )
15	--	171.36 (C)